

Co-deposition mechanism of trace Cu and Fe on H-Si(100) surface in buffered fluoride solutions

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Wet treatment of wafers with aqueous fluoride solution is a fundamental process for silicon device manufacturing. In this process, spontaneous deposition of trace metal contaminant included in the solutions is one of the critical issues and numbers of studies have been carried out to elucidate its mechanism, mainly focusing upon the deposition processes of single metal species [1-3]. On the other hand, we have found the interaction on the deposition of two trace metal species co-existing in the solution on H-Si(111) surfaces [4]. We have also investigated the deposition mechanism of trace metals on the silicon wafers as well as the corrosion mechanisms of the wafers in aqueous fluoride solutions [5-7].

Based upon these results, in the present work, interaction effect and co-deposition mechanism of trace Fe and Cu co-deposition on silicon wafer surface in aqueous NH₄F solution was investigated in detail.

P-type Si(100) wafers (9-18 Ω cm) were used for the present work. The wafers were cleaned with a mixture of 4:1 96% H₂SO₄ : 30% aqueous H₂O₂ for 10 min at 120°C, followed by rinsing with ultra pure water. Then the wafers were immersed for 1 min in 0.5 % aqueous HF to prepare clean, hydrogen terminated surface, followed by immersing into the NH₄F solution (Ultrapur^(R) or SLSI grade) containing controlled amount of Cu and/or Fe. The wafers were then observed using a tapping mode atomic force microscope (TMAFM). Amounts of the metals deposited on the wafer surface were measured using a total reflection X-ray fluorescence spectrometer (TXRF). Electrochemical analyses, such as anodic stripping voltammetry (ASV) and open circuit potential (OCP) measurement were carried out for detailed investigation of the interaction mechanism of the trace metal species, using either the silicon wafer or a glassy carbon electrode.

Figure 1 shows representative TMAFM images for the wafers immersed into the NH₄F solution containing trace metal species. The TXRF measurements for deposited amounts of the metals on the surface clarified the enhancement of the trace Fe deposition on Si wafer in the presence of trace Cu; in the case of the Fe single-spiked condition (Fe 50 ppb: the condition same as Fig. 1a), the deposited amount of Fe was 1.4×10^{11} atoms/cm², whereas it increased to 3.2×10^{11} atoms/cm² in the presence of Cu (Fe 50 ppb + Cu 20 ppb: the condition same as Fig. 1c).

In order to elucidate its origin, electrochemical analyses were carried out. Since the silicon surface is quite active in the NH₄F, dissolution and hydrogen evolution occurs at anodic and cathodic potentials respectively. Thus, as a fundamental investigation, the ASV was carried out using glassy carbon electrode to focus the interaction between two metallic ion species and to eliminate the effect of silicon surface activity. The ASV results suggested the formation

of Cu-Fe alloy at the potential equal to the open circuit potential of Si wafer immersed into NH₄F. In this case, the deposition potential shifts toward anodic direction, indicating that the deposition is enhanced if Cu coexisted with Fe. Such an alloying effect could be one of the origins of the co-deposition effect.

On the other hand, effect of the catalytic activity of the surface site, where the trace Fe deposition takes place, should be also considered. The deposition potential of trace Fe in the NH₄F solution on (i) clean Si wafer, (ii) clean Si wafer with Fe particle (the surface shown in Fig. 1a), and (iii) clean wafer with Cu particle (the surface shown in Fig. 1b) was measured. It turned out that the (iii) possessed the most positive potential, indicating that the rate constant for electron transfer leading to the electrochemical deposition of Fe is higher on Cu nuclei than on Si substrate, which could be another origin of the co-deposition effect.

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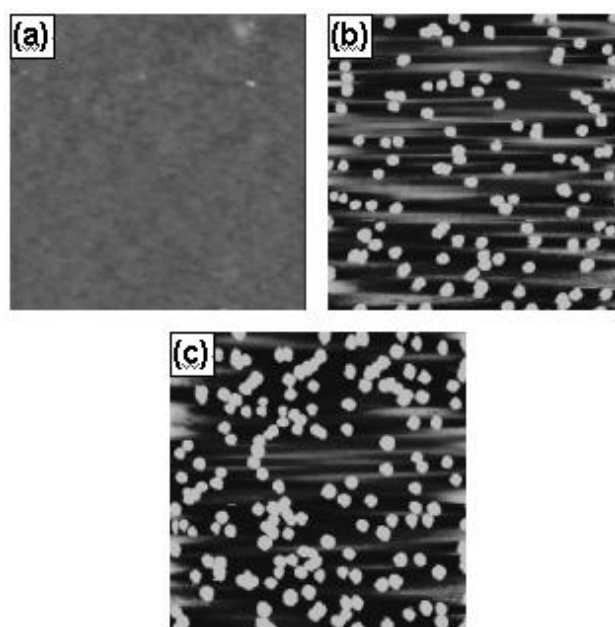


Figure 1 TMAFM images of Si(100) wafers immersed in Ar-sparged 40% NH₄F with (a) 50 ppb of Fe SO₄, (b) 20 ppb of Cu SO₄, (c) 50 ppb of Fe SO₄ + 20 ppb of Cu SO₄ for 5 min. Scan area: 1.0 μ m x 1.0 μ m; Vertical scale: from 0nm (black) to 10 nm (white).